Sandwich-Like Complexes Based on "All-Metal" (Al₄²⁻) Aromatic Compounds

Jose M. Mercero* and Jesus M. Ugalde

Kimika Fakultatea, Euskal Herriko Unibertsitatea, P. K. 1072 20080 Donostia, Euskadi, Spain

Received October 15, 2003; E-mail: pobmelat@sq.ehu.es

Designing new chemical compounds is one of the most ambitious goals of every chemist. Nonetheless, efforts made to understand the chemistry of new chemical compounds often yield new paradigms which open unexpected research areas. All-metal aromatic molecules, recently synthesized by Li et al.,[1] constitute one such example. Indeed, rationalizing the unexpected large resonance energy of Al_4^{2-} has yielded the concept of multiple-fold aromaticity,[2−5] present in molecules that possess more than one independent delocalized bonding system, either σ-type or π-type, each of them satisfying the $4n + 2$ electron counting rule of aromaticity. This new concept should help one to understand the simultaneous contributions to aromaticity within the same molecular structure as arising from various delocalized bonding systems of the molecule, and it should be of general applicability, irrespective of whether the molecule is organic or inorganic.

The all-metal aromatic Al_4^{2-} molecule, therefore, is the first of the series of recently synthesized compounds that constitute a new paradigm in chemistry.[4−6] These compounds present properties similar to those of Al_4^{2-}, high magnetic shielding,[7] large ring current,[8] similar derived antiaromatic structures,[9] and large resonance energies.[2,5]

These molecules are normally prepared as singly charged anions because doubly charged species are expected to be rather unstable in the gas phase due to large intramolecular Coulomb repulsion. Thus, complexation with counterions is required to produce more stable species and is also convenient for mass analysis and photodetachment experiments. However, as recently stated by Kuznetsov et al.,[10] "...the question remains if the X_4^{2-} aromatic rings can be incorporated into sandwich-type complexes...", but, as far as we know, no sandwich-type complexes of these molecules have been reported to date.

We have focused on this idea and have been able to calculate stable sandwich-type structures which have a structure similar to that of metallocenes. The $Al_4TiAl_4{}^{2-}$ has two aromatic −2 charged squares (analogous to the cyclopentadienyls in the metallocenes) and a +2 charged titanium on the center of the system (see Figure 1; note that all of the figures were made using the MOLDEN[11] program).

The B3LYP functional, as implemented in Gaussian 98,[12] with a selected standard 6-311G basis set was employed for the calculations. The results with larger basis sets are available as Supporting Information.

The minima has a staggered form, with D_{4d} symmetry. We have also found the eclipsed isomer, which turns out to be the transition state for the staggered isomer's interconversion, only 5 kcal/mol higher in energy. The main geometrical parameters of the minimum energy structure are collected in Table 1. Inspection of the Al_4^{2-} moiety reveals that the Al−Al bond lengths elongate 0.14 Å upon complexation.

This molecule has two-fold degenerate HOMO (e_3) and LUMO (e_1) orbitals (shown in the Supporting Information).
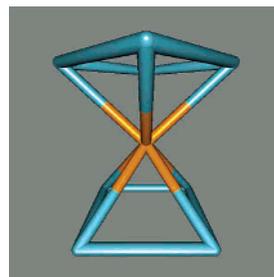
Figure 1. $Al_4TiAl_4{}^{2-}$ molecule.

Table 1. The Properties of the Molecules (Calculated at the B3LYP/6-311G Level of Theory) Described in the Text[a]

	$Al_4TiAl_4{}^{2-}$ (D_{4d})		Al_4^{2-} (D_{4h})
R_{C-Ti}	1.900		
R_{Al-C}	1.977		1.881
BE	−607.13		
NICS (0)	−39.02		−28.48
NICS (1)	−16.93		−24.15
$EDE_v^{b_2}$	−0.558	$EDE_v^{b_{2g}}$	−1.739
$EDE_a^{b_2}$	−0.633	$EDE_a^{a_g}$	−1.948
$EDE_{ovg}^{b_2}$	−1.001 (1.00)	$EDE_{ovg}^{b_{2g}}$	−1.250 (0.88)

[a] The bond lengths are given in angstroms. Binding energies are reported in kcal/mol and EDEs are in eV, with the pole strengths in parentheses. The v, a, and ovg subscripts describe how the EDE was evaluated: vertical, adiabatic, and outer valence green functions EDEs, respectively, and the superscript describes the orbital from where the electron is detached. The NICS values are given in ppm.

The electron detachment energy (EDE) gives an indication of the stability of the dianion. The vertical[13] (EDE_v) and adiabatic[14] (EDE_a) detachment energies, along with those calculated using the OVGF (EDE_{ovg}) (outer valence green functions unrestricted implementation of Gaussian 98),[15] are given in Table 1. All of these methods report negative values of the EDEs, indicating that the monoanion is more stable than the dianion. Note that the same was found for the $Al_4{}^{2-}$ square,[2] where the monoanion is more stable by −1.52 eV. The electron detachment process occurs from the HOMO−2, b_2 orbital (see Supporting Information), yielding a "nondegenerate" doublet monoanion.

Fragmentation of the molecule is another possibility in which one may spatially separate the charges. To check this possibility, we have calculated the fragmentation energy in the following way:

$$Al_4TiAl_4{}^{2-} \rightarrow 2Al_4{}^{2-} + Ti^{2+} \qquad (1)$$
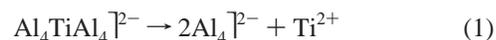
where the titanium(II) cation results in the ^1D state.

The fragmentation of this molecule will not occur easily, because the binding energy is large, around 610 kcal/mol. This value is similar to metallocene binding energies. The ferrocene experimental binding energy is 635 ± 6 kcal/mol, and the calculated values are around 656 kcal/mol at a similar theory level.[16]

The nucleus-independent chemical shift (NICS) is a feasible index of the aromaticity of a molecule.[17] We have calculated the

found in the isolated $NaAl_4^{1-}$, and also similar to the dianion sandwich. The NICSs and the EDEs have also been calculated. The NICS values are similar to the $Al_4TiAl_4^{2-}$ values (see Table 2).

Finally, in the $NaAl_4TiAl_4Na$ neutral molecule, the sodium atoms (as in the $NaAl_4TiAl_4^{1-}$ anion) are out of the Al_4 square planes, and the deformation of the rings is slightly larger than that in the monoanion. All of the properties of these compounds support the idea that Al_4^{2-} aromatic squares are present.

The structures predicted here await experimental verification.

Supporting Information Available: Summary of the coordinates and properties of the compounds obtained with larger basis sets (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 2. $NaAl_4TiAl_4^{1-}$ and $NaAl_4TiAl_4Na$ structures.

Table 2. Properties of the Sodium-Containing Complexes[a]

	$NaAl_4TiAl_4^{1-}$ (C_1)	$NaAl_4TiAl_4Na$ (C_1)
$R_{C-Ti}/(Na)$	1.920 *(1.890)*	1.80
BE	−578.02	−487.32
NICS (0)/(Na)	−38.5 *(−39.27)*	−37.0/−14.9
NICS (1)/(Na)	−17.93 *(−16.98)*	−16.50
EDE_v	1.997	
EDE_a	1.849	
EDE_{ovg}^{HOMO}	1.891 (1.00)	

[a] See the footnote of Table 1. The values in italics correspond to the square interacting with the sodium atom.

NICS of the aromatic squares at different points around the Al_4 squares before and after the metallocene-like molecule was formed. Thus, the NICS has been calculated in the center of the square (NICS (0)), and in the normal of the square (NICS (1)). The Al_4^{2-} square has NICS (0) and NICS (1) values of −28 and −24 ppm, respectively. Once in the complex, the new values are −39 and −17 ppm. The signs of the NICSs remain negative, indicating that the aromatic character of the squares remains upon complex formation. Thus, it is fair to say that the complex has an aromatic−metal−aromatic structure.

Al_4^{2-} has been experimentally detected interacting with another metal cation; therefore, we have calculated a similar sandwich complex in the presence of a sodium atom (a molecule with charge −1, as the experimentally detected species[1]), and with two sodium atoms, using the experimentally detected $NaAl_4^{1-}$ molecule as the building block (see Figure 2). The properties of these complexes are sumarized in Table 2.

The $NaAl_4^{1-}$ unit found in the $NaAl_4TiAl_4^{1-}$ differs from those described by Li et al.[1] They characterized one planar and another pyramidal structure for $NaAl_4^{1-}$ and suggested that the global minimum corresponds to the pyramidal form. In the $NaAl_4TiAl_4^{1-}$ anion, the Na is out of the Al_4 plane, and it is not forming a pyramid. The distance between Na and the closest two Al is similar to that

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JA039074B